Final Report for AOARD Grant FA 4869-07-1-4090 "**Lithium-air Battery Research**"

December 2009

Name of Principal Investigators: Prof. N. Munichandraiah

- e-mail address : muni@ipc.iisc.ernet.in
- Institution : Indian Institute of Science, INDIA
- Mailing Address : Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore- 560012, India
- Phone : +91-80-2293-3183
- Fax : +91-80-2360-0683, 2360-1552

Period of Performance: From 12 November 2007 to 11 November 2009

Abstract: Lithium-air battery is considered as one of the highest energy density batteries for various future applications. There are only limited studies reported in the literature on this battery system. In the present project studies, various aspects related to fabrication of air electrode and assembly of Li-air (or, oxygen) cells are undertaken. Firstly, several carbon samples are screened to fabricate air electrodes, and they are tested by assembling Li-air cells in cell containers suitably made for this purpose. Carbon sample, which is purchased from a China company is found to provide a maximum discharge capacity. Further experiments are conducted to optimize the conditions of electrodes preparation, evaluate various catalysts for oxygen electrode, etc. Using optimized air electrodes, it is found that a maximum discharge capacity of 3000 mAh/g can be obtained for Li-air cell. This value is one of the highest capacity values reported so far in the literature. The various experiments conducted and the results obtained are reported here.

Introduction: Research on lithium-air battery is interesting as its cathode utilizes oxygen in air free of cost. Infinite availability of oxygen in air and no need to store it inside the battery are attractive features of the Li-air battery. It is anticipated that the specific energy of Li-air battery would be about 400 – 500 Wh / kg against about 200 Wh / kg achieved for Li-ion battery. There is very little work done so far on this battery system. The physical structure of carbon such as surface area, porosity, wettability or hydrophobicity, etc. and the catalyst decide the performance of the cathode. In the present studies, various carbon samples are evaluated for their suitability to use as air-electrodes. The experimental parameters such as the type of binder, the amount of binder, etc., are studied to achieve a maximum discharge capacity. Rechargeability of Li-air cells is studied.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
07 JAN 2010	**FInal**	**29-09-2007 to 28-09-2009**

4. TITLE AND SUBTITLE
Lithium-Air Battery Research

5a. CONTRACT NUMBER
FA48690714090

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Munichandraiah Nookala

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Indian Institute of Science,Department of Inorganic and Physical Chemistry,Bangalore 560 012,India,IN,560012

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AOARD, UNIT 45002, APO, AP, 96337-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AOARD

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AOARD-074090

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Lithium-air battery is considered as one of the highest energy density batteries for various future applications. There are only limited studies reported in the literature on this battery system. In the present project studies, various aspects related to fabrication of air electrode and assembly of Li-air (or, oxygen) cells are undertaken. Firstly, several carbon samples are screened to fabricate air electrodes, and they are tested by assembling Li-air cells in cell containers suitably made for this purpose. Carbon sample, which is purchased from a China company is found to provide a maximum discharge capacity. Further experiments are conducted to optimize the conditions of electrodes preparation, evaluate various catalysts for oxygen electrode, etc. Using optimized air electrodes, it is found that a maximum discharge capacity of 3000 mAh/g can be obtained for Li-air cell. This value is one of the highest capacity values reported so far in the literature. The various experiments conducted and the results obtained are reported here.

15. SUBJECT TERMS
Batteries, lithium-air battery, discharge capacity

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**Same as Report (SAR)**	**32**	

Detailed Description of the Project with Analytical/Experimental work:

Cells are machined out of Teflon and tested for their suitability for fabrication of Li-air cells. The photographs of the cell and experimental set up are shown in Figures 1 and 2. The following five types of carbons are tested for their suitability for air-electrodes: (i) Super P carbon, (ii) Super PLi carbon, (iii) Lonza graphite, (iv) KS10 graphite and (v) China carbon.

For preparation of carbon air electrodes, carbon powder and a binder (Teflon suspension (PTFE) or polyvinyledene fluoride (PVDF)] are mixed together and subjected to grinding thoroughly. In the case of PTFE binder, the powder becomes a dough which was rolled into a thin sheet. In the case of PVDF, a few drops of solvent, n-methyl pyrrolidinone (NMP) are added to get a syrup. Ni mesh of 12 mm dia is sectioned out of a sheet of mesh, etched in dil-H_2SO_4 and dried. Carbon mixed with binder is applied on Ni mesh, pressed under hydraulic press, and dried. Cells are assembled in argon filled glove box employing lithium foil as the anode and 1.0M $LiPF_6$ dissolved in propylene carbonate as the electrolyte. Cells are taken out of the glove box and an oxygen filled bulb is connected to carbon electrode. Cells are allowed to rest for about three hours and then subjected to charge-discharge cycling by passing a constant current through the cell. Discharge capacity values are calculated in the units of mAh/g. The mass of carbon is used for calculation of specific discharge capacity.

Results and Discussion:

(i)Studies on selection of carbon samples:

The charge-discharge cycles of Li-air cells made with Super P carbon with a current of 0.5 mA are shown in Figure 3(A). The initial discharge time is large, and the time decreases on repeating the charge-discharge cycles. The discharge capacity versus cycle number is shown in Figure 3(B). The capacity obtained for the first discharge is about 70 mAh/g. There is a decrease in capacity to about 2 mAh/g for the second discharge and thereafter it remains at the same low value.

Similar to the above data for Super P carbon, the data of charge-discharge and cycling capacity for Super PLi, Lonza graphite, KS10 graphite and China carbon are shown in Figures 4-7, respectively. The maximum discharge capacity values obtained for these samples are 180, 18, 130 and 135 mAh/g, respectively. However, except in the case of China carbon, for all samples the discharge capacity decreases drastically for the second cycle. For China carbon, the capacity remains at reasonably high values for 6 cycles, then it decreases to about 70 mAh/g and remains at this value for cycles up to ten. In order to study the effect of binder used for electrode fabrication, some electrodes were made with PVDF as the binder and tested. The data measured are shown in Figure 8. The initial capacity is only about 30 mAh/g and it decreases gradually on repeated charge/discharge cycling.

From the above experimental results, it is concluded that China carbon is more suitable for Li-air battery application than the rest of the samples, and also PTFE is better than PVDF as the binder. Further experiments on enhancing capacity and cycle life by employing several catalysts are in progress.

(ii) Studies on optimization of binder content:

High surface area china carbon is used to prepare air electrodes with PTFE suspension as the binder. The amount of binder is varied to study its effect on discharge capacity and rechargeability of Li-air cells. The cells are assembled in Teflon cell holders using non-aqueous electrolyte of $LiPF_6$ in propylene carbonate (PC). The cells are subjected to ten charge-discharge cycles with 0.5 mA current (14 mm diameter electrodes). The data are presented in Figures 9-13. It is seen that for all levels of the PTFE binder from 5 wt% to 15 wt%, the data appear almost similar. The capacity measured for the initial discharge is about **150 to 200 mAh/g** (based on mass of carbon powder) and thereafter the discharge capacity decreases on repeated charge – discharge cycling.

(iii) Two – layer approach (Active layer and Diffusion layer):

For the purpose of enhancing discharge capacity of Li-air cell from the values of about 200 mAh/g so far measured, an approach attempted is to prepare the air electrode with two layers of carbon. The carbon – layer, which is exposed to the electrolyte consists of smaller amount of carbon with a catalyst and the carbon – layer present towards the oxygen side is made of greater amount of carbon but without the catalyst. Several electrodes are made by varying the binder in diffusion – layer and cells are assembled. The charge – discharge cycling data are presented in Figures 14-17. It is interesting to observe that the discharge capacity of about **1100 mAh/g** is obtained when the active layer is made of 5 wt% PTFE with the diffuse layer made of 30 to 50 wt% (capacity values are based on only active layer carbon mass).

(iv) The effect of binder amount in active layer:

Experiments are conducted by keeping the binder at 30 wt% in the diffusion - layer and varying the binder in the active layer of the air electrodes. The results are presented in Figures 18 – 22. It is observed that the discharge capacity is about 1000 mAh/g when the active layer contains 30 wt% binder. The high discharge capacity values are measured only after adopting two – layer approach. Hence the subsequent experiments are conducted with this electrode configuration.

(v) Effect of electrolytes:

So far, the experiments are conducted in propylene carbonate solvent and LiPF6 as the salt for the electrolyte. It is intended to examine the effect of nature of the solvent on performance of Li – air cells. Gel polymer electrolyte, propylene carbonate + ethylene carbonate (1:1) mixture, propylene

carbonate + diethyl carbonate (1:1) mixture and propylene carbonate + dimethyl carbonate (1:1) mixture are employed with $LiPF_6$ as the salt. For these experiments Swagelok type cells are employed (Figure 2). The data are presented in Figures 23 - 28. It is seen that the discharge capacity as high as **3000 mAh/g** is obtained in propylene carbonate + dimethyl carbonate containing 1.0 M $LiPF_6$ as the electrolyte.

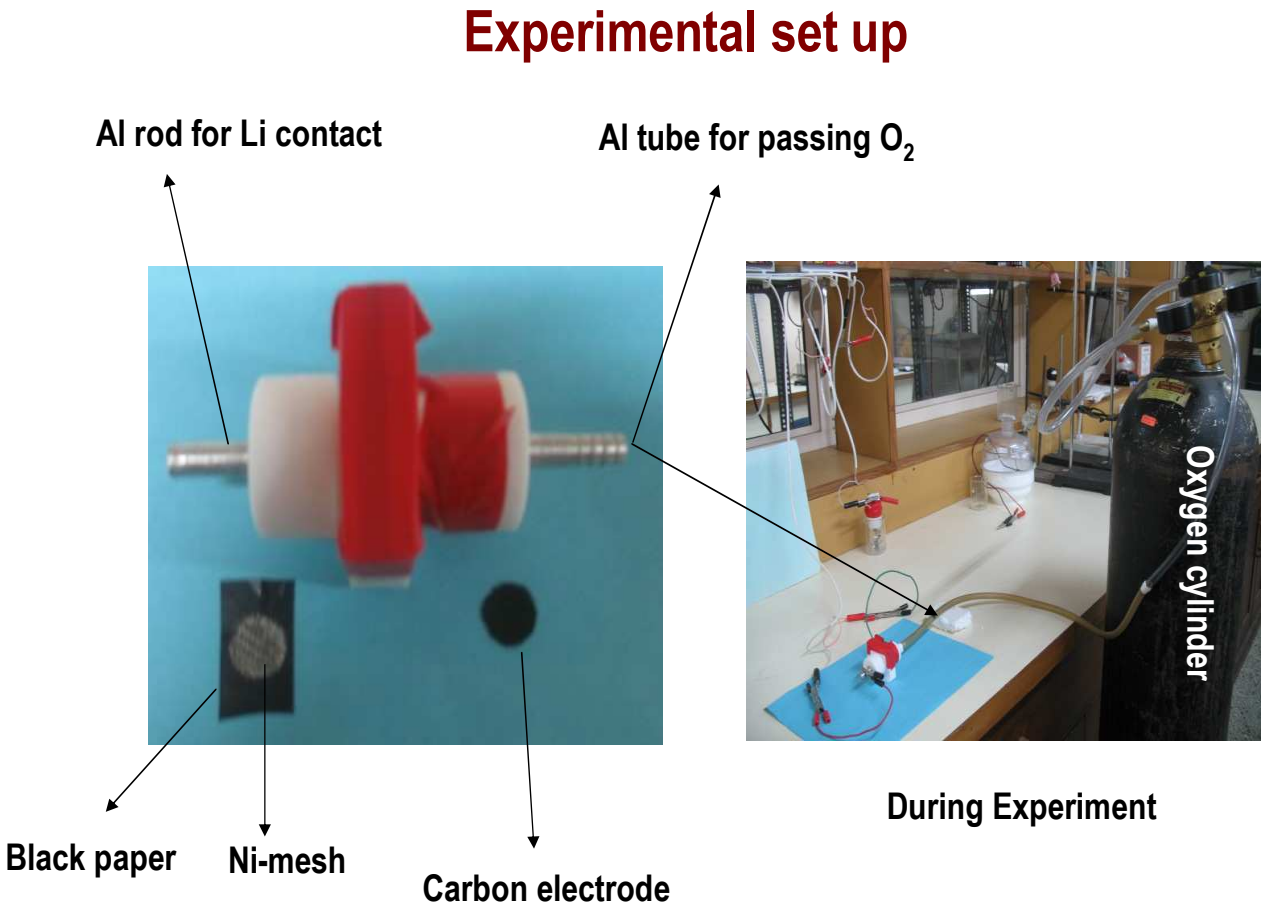

Figure 1 Home made Teflon cell assembly

Figure 2: Home made Swagelok – type cell assembly

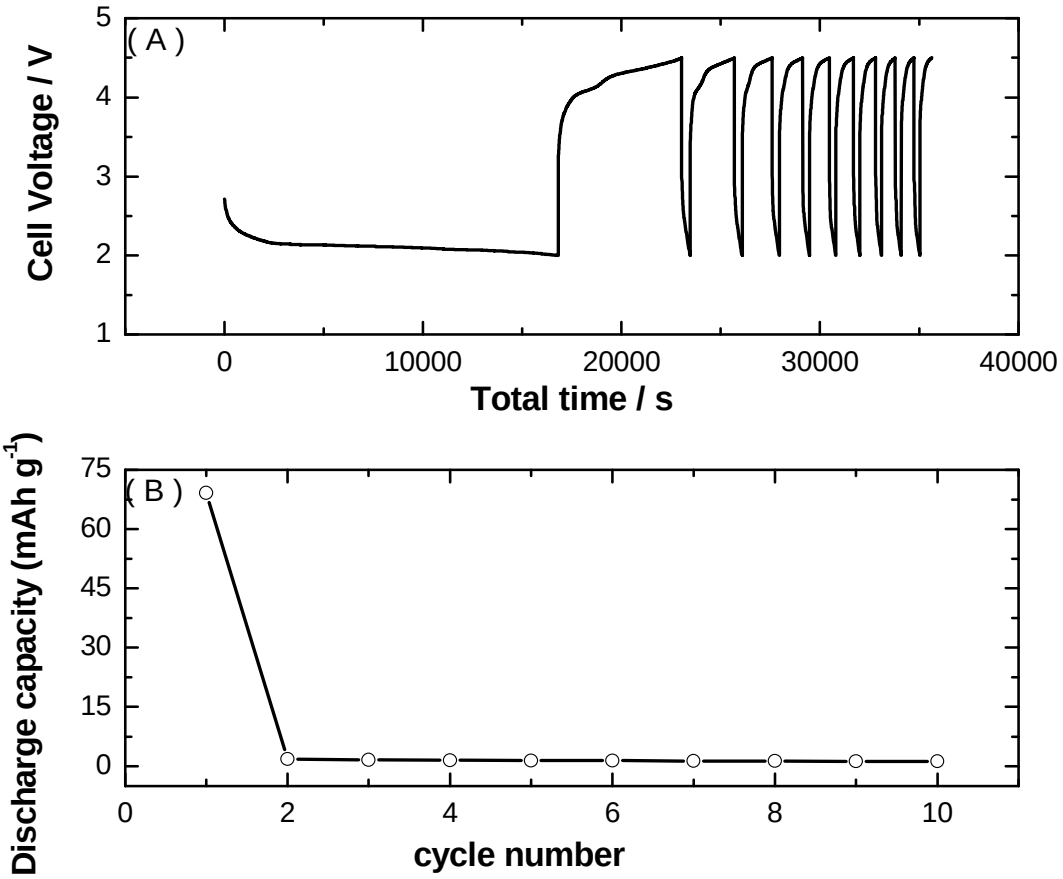

Figure 3. Charge-discharge cycling of Li-air cell made out of Super P carbon ; current : 0.5 mA

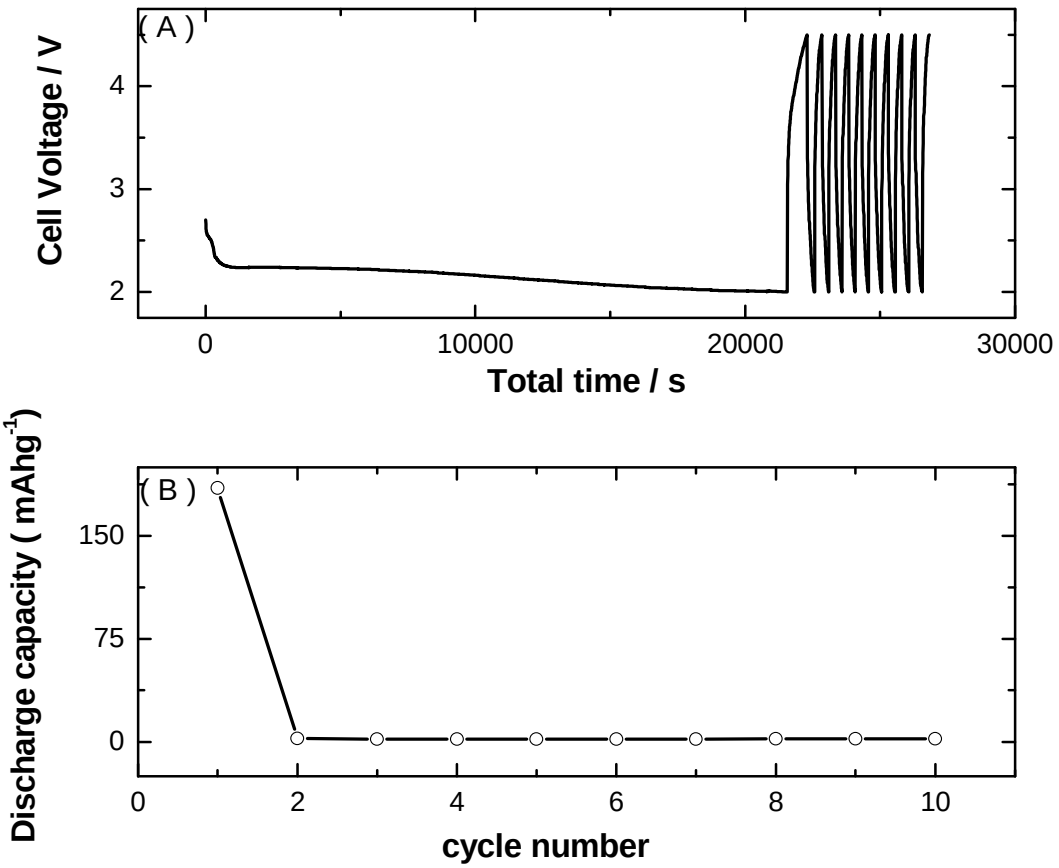

Figure 4. Charge-discharge cycling of Li-air cell made out of Super PLi carbon ; current : 0.5 mA

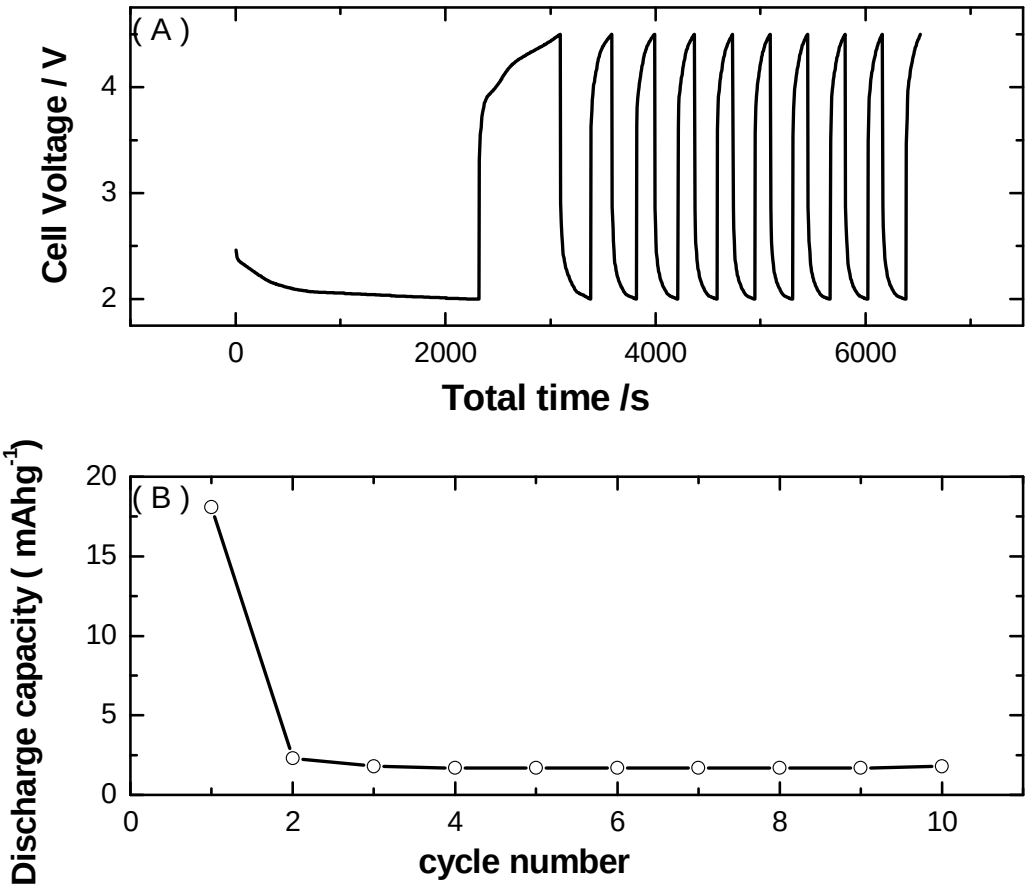

Figure 5. Charge-discharge cycling of Li-air cell made out of Lonza graphite ; current : 0.5 mA

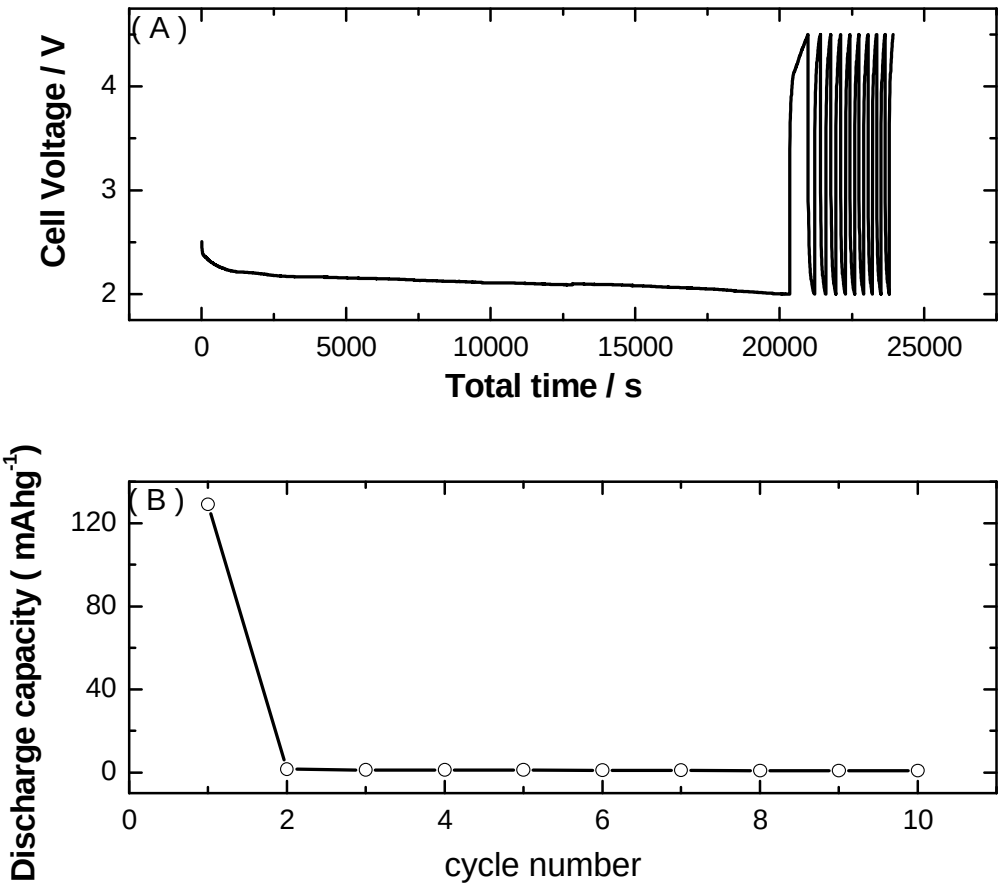

Figure 6. Charge-discharge cycling of Li-air cell made out of KS 10 graphite ; current : 0.5 mA

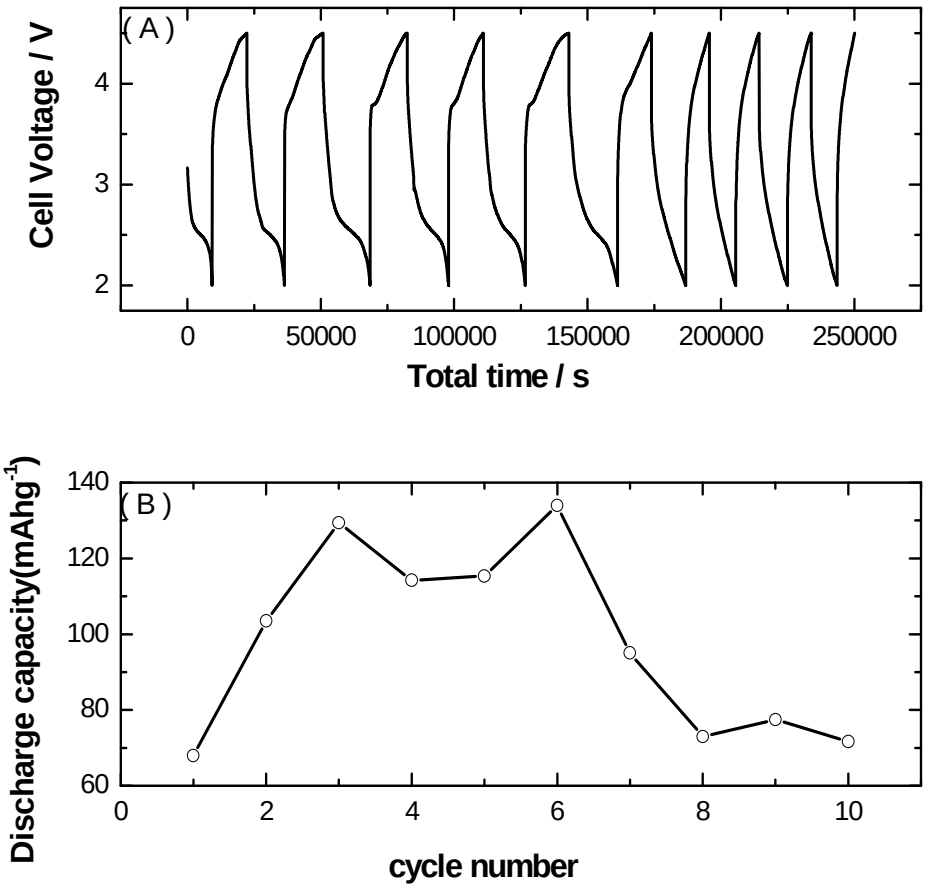

Figure 7. Charge-discharge cycling of Li-air cell made out of China carbon ; current : 0.5 mA

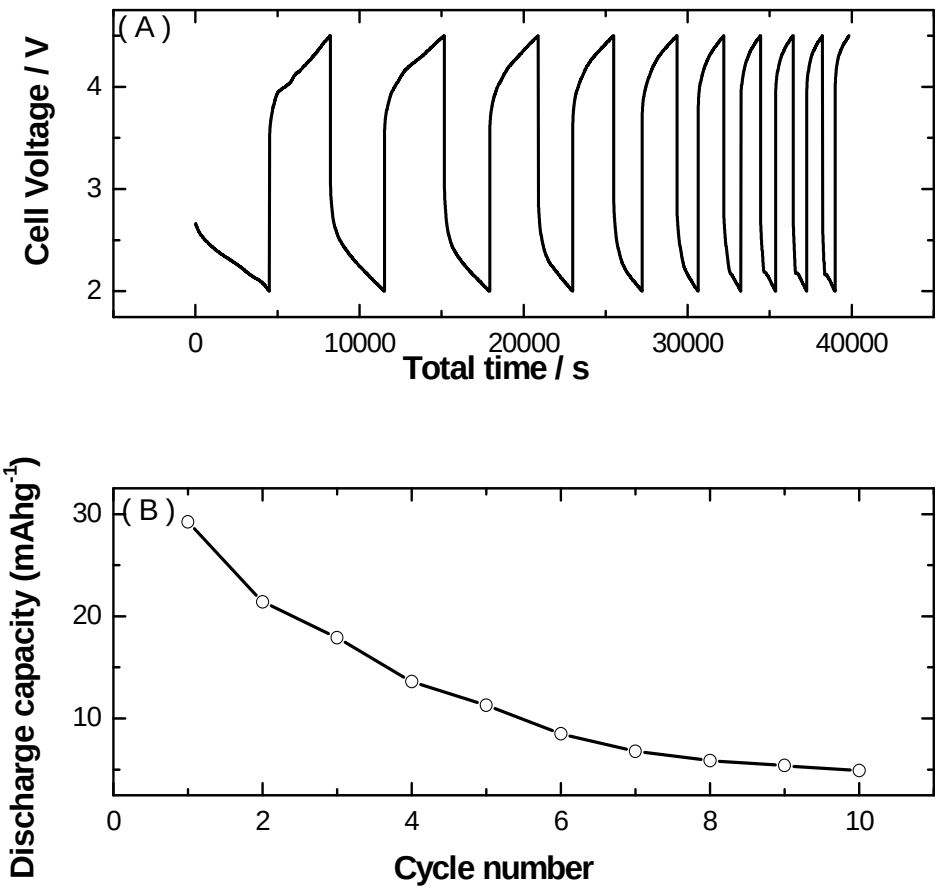

Figure 8. Charge-discharge cycling of Li-air cell made out of China carbon with PVD binder ; current : 0.5 mA

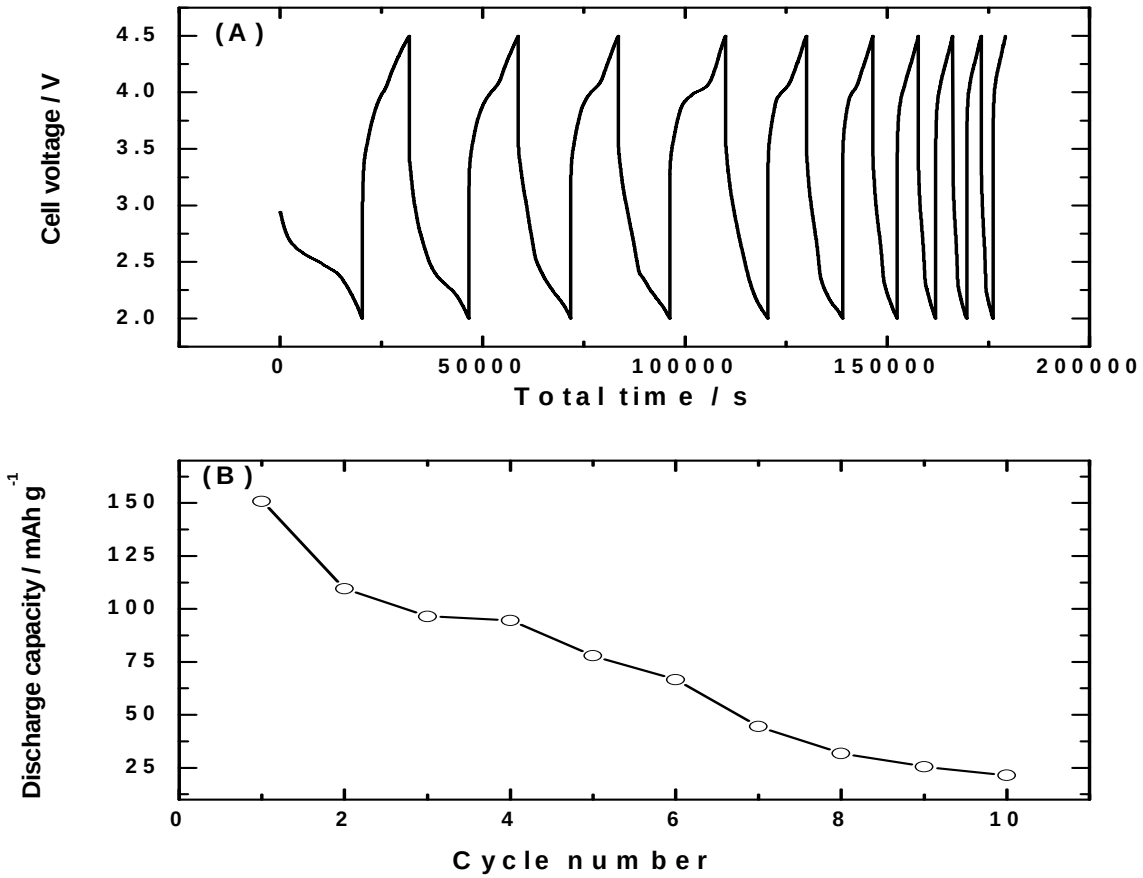

Figure 9 : Cell No: TF 92 ;
Carbon 95 wt% + PTFE 5 wt% ;
Carbon : 18.7 mg ;
Area : 1.5 cm^2 ;
Single layer;
Discharge – charge current : 0.5 mA;
No catalyst.

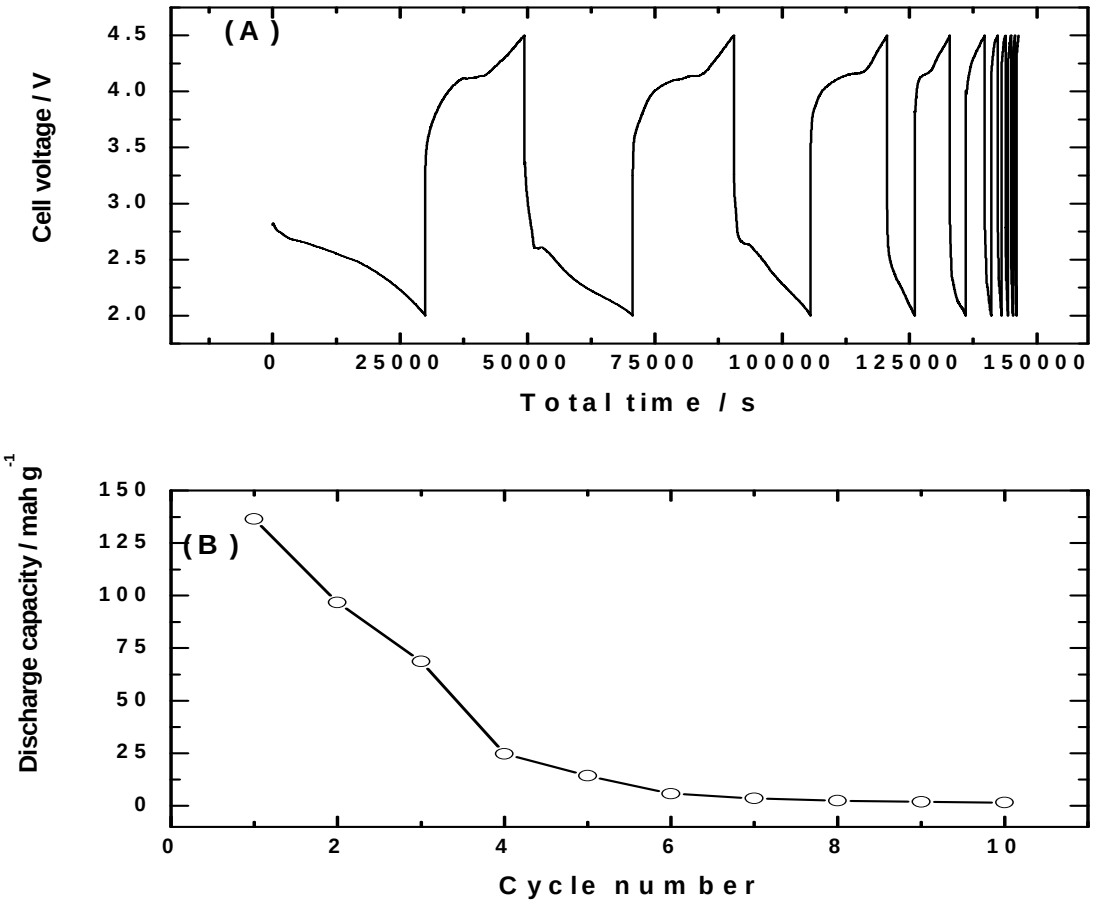

Figure 10 : Cell No: TF 97 ;
Carbon 92.5 wt% + PTFE 7.5 wt% ;
Carbon : 30.59 mg ;
Area : 1.5 cm^2 ;
Single layer;
Discharge – charge current : 0.5 mA;
No catalyst.

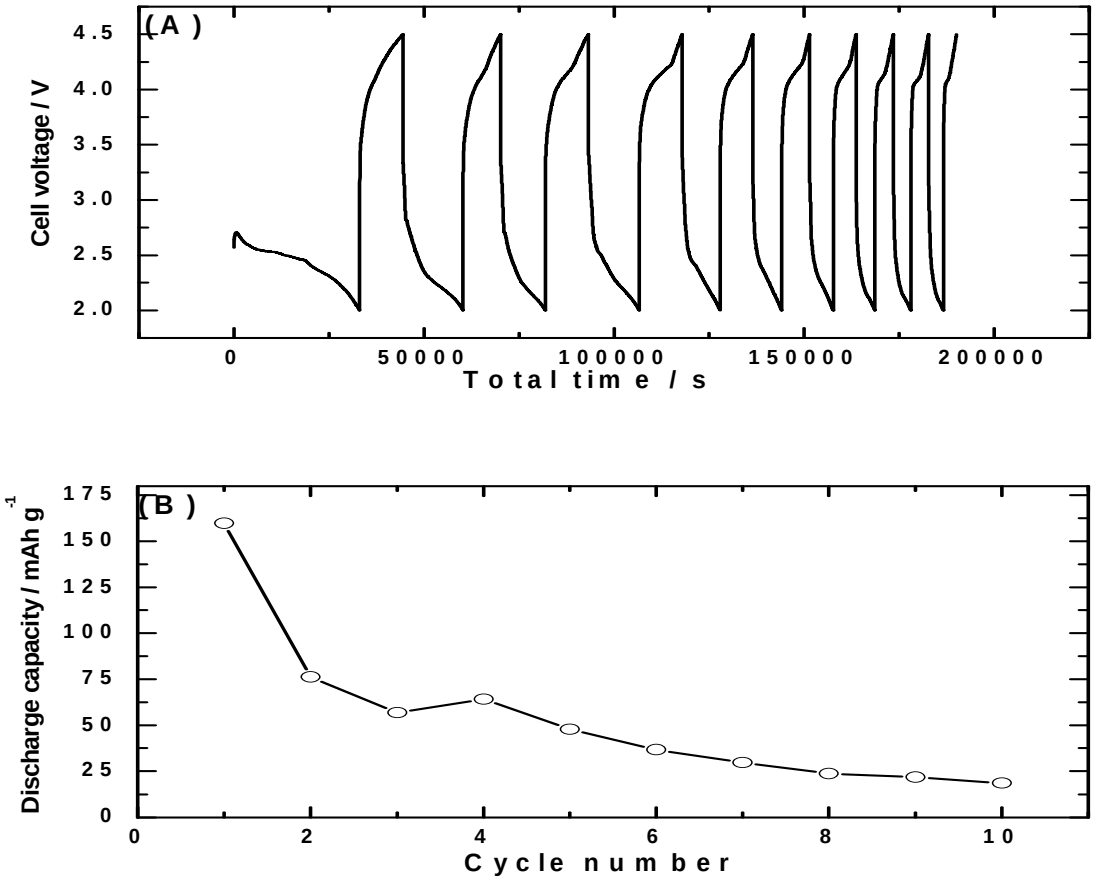

Figure 11 : Cell No: TF 98 ;
Carbon 90 wt% + PTFE 10 wt% ;
Carbon : 28.8 mg ;
Area : 1.5 cm^2 ;
Single layer;
Discharge – charge current : 0.5 mA;
No catalyst.

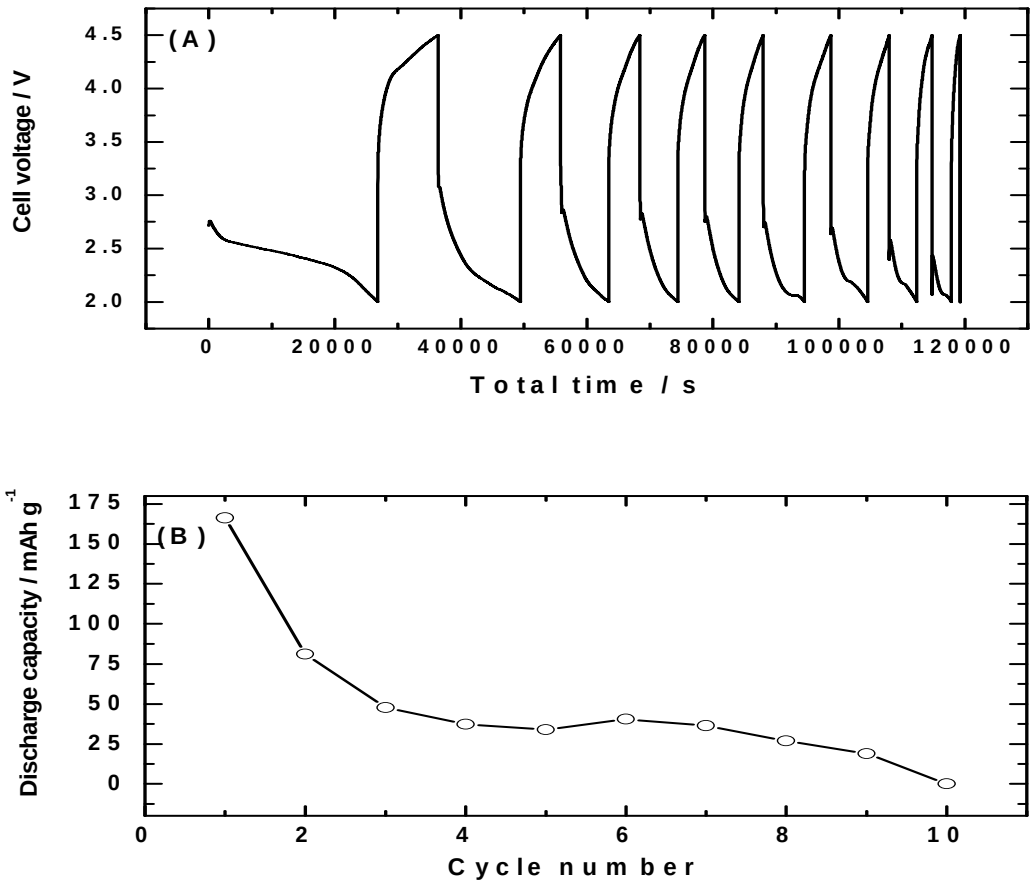

Figure 12 : Cell No: TF 101 ;
Carbon 87.5 wt% + PTFE 12.5 wt% ;
Carbon : 22.48 mg ;
Area : 1.5 cm^2 ;
Single layer;
Discharge – charge current : 0.5 mA;
No catalyst.

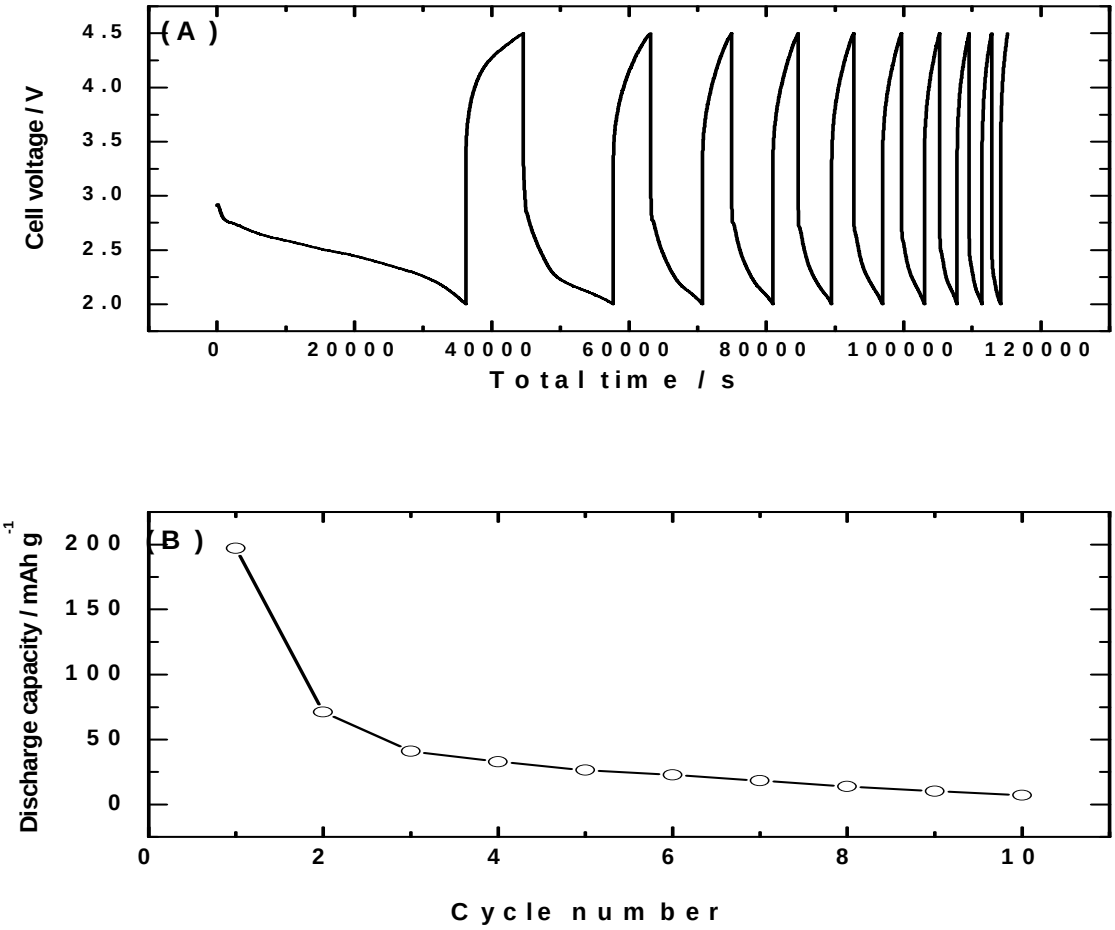

Figure 13: Cell No: TF 103 ;
Carbon 85 wt% + PTFE 15 wt% ;
Carbon : 25.5 mg ;
Area : 1.5 cm^2 ;
Single layer;
Discharge – charge current : 0.5 mA;
No catalyst.

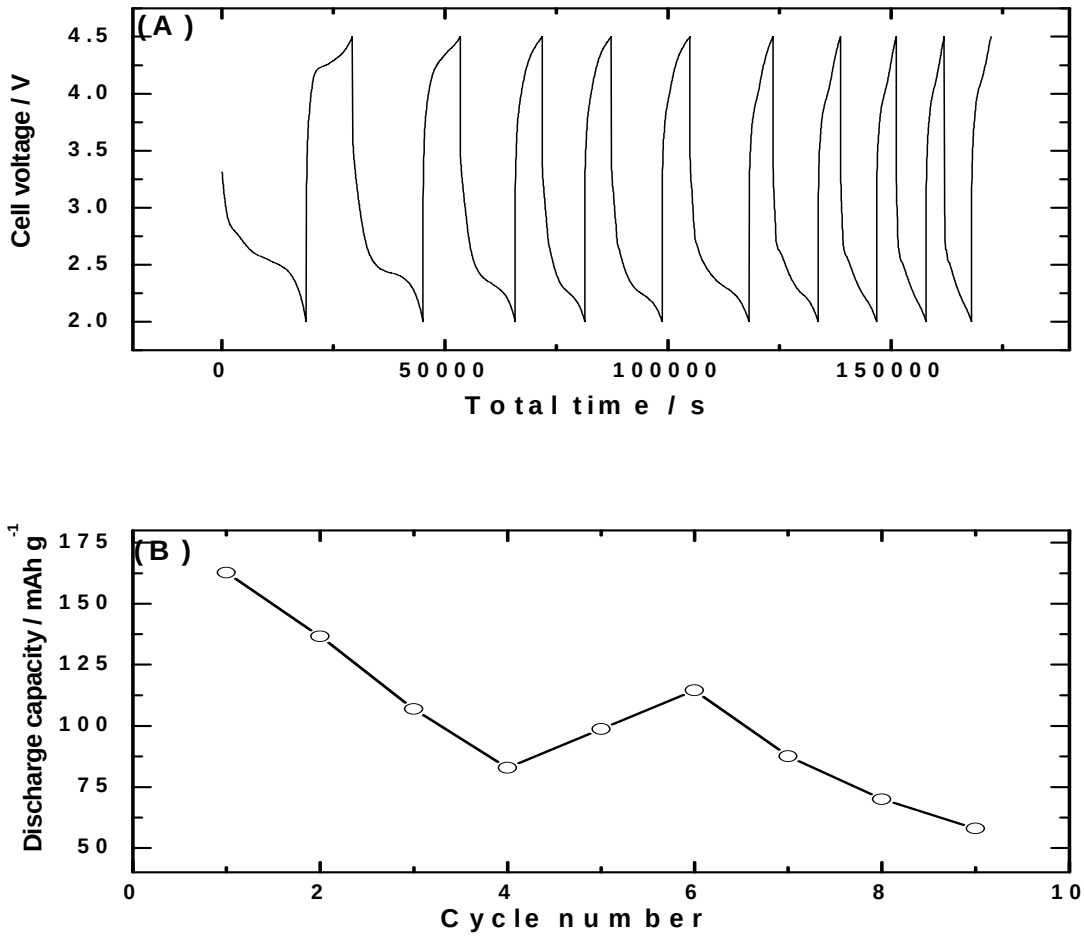

Figure 14 : Cell No: TF 207 ;
Active layer carbon : 16.13 mg;
Diffusion layer carbon : No diffusion layer ;
Amount of PTFE in diffusion layer : Nil ;
Discharge – charge current : 0.5 mA;

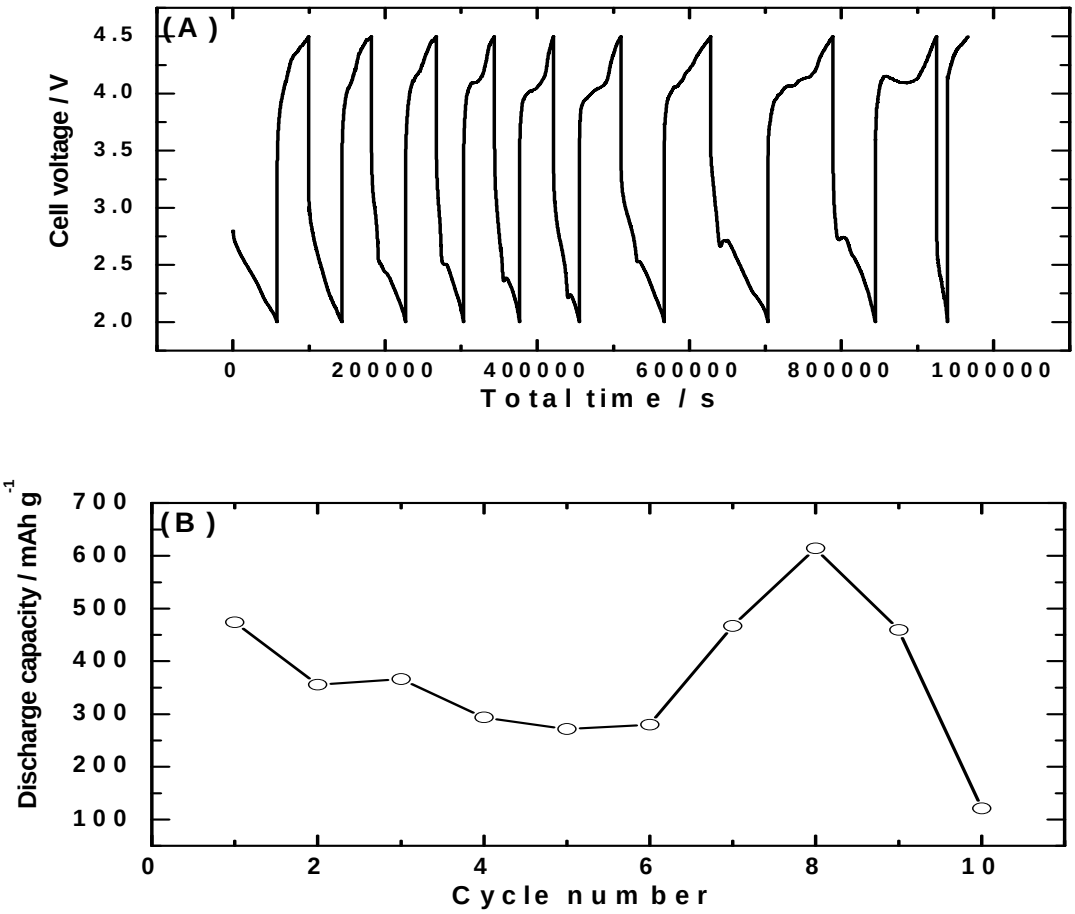

Figure 15: Cell No: TF 163 ;
Active layer carbon : 17.07 mg;
Diffusion layer carbon : 161.2 mg ;
Amount of PTFE in active layer : 5 wt% ;
Amount of PTFE in diffusion layer : 30 wt% ;
Discharge – charge current : 0.5 mA;

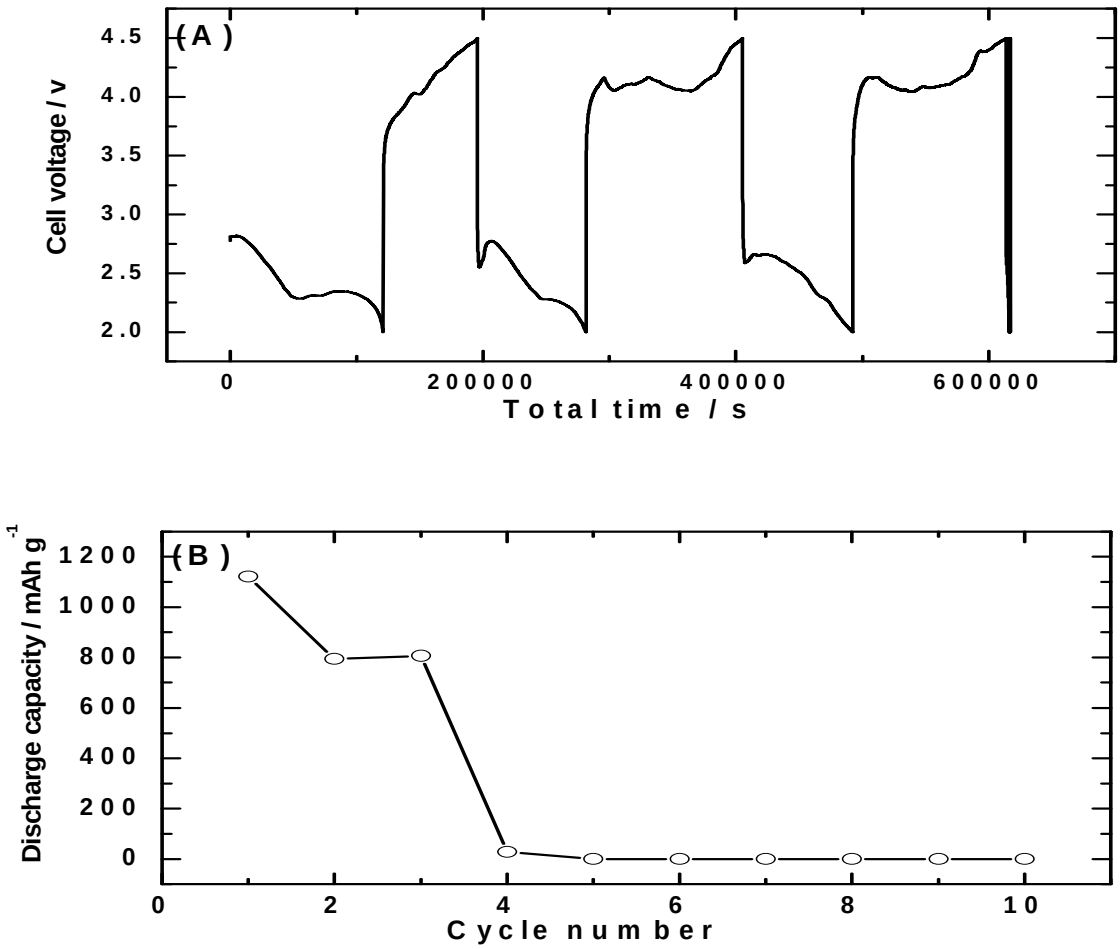

Figure 16 : Cell No: TF 164 ;
Active layer carbon : 15.4 mg;
Diffusion layer carbon : 261.3 mg ;
Amount of PTFE in active layer : 5 wt% ;
Amount of PTFE in diffusion layer : 40 wt% ;
Discharge – charge current : 0.5 mA;

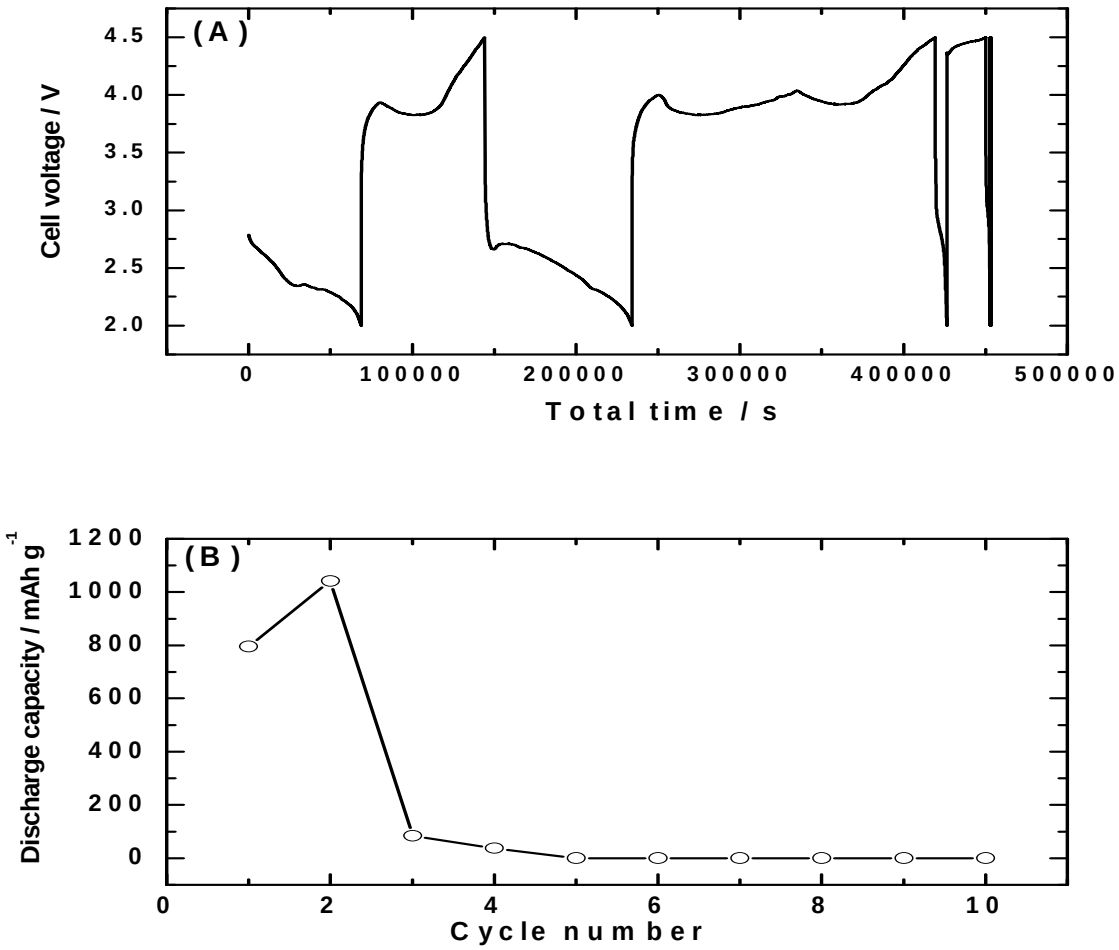

Figure 17 : Cell No: TF 167 ;
Active layer carbon : 12.57 mg;
Diffusion layer carbon : 281.36 mg ;
Amount of PTFE in active layer : 5 wt% ;
Amount of PTFE in diffusion layer : 50 wt% ;
Discharge – charge current : 0.5 mA;

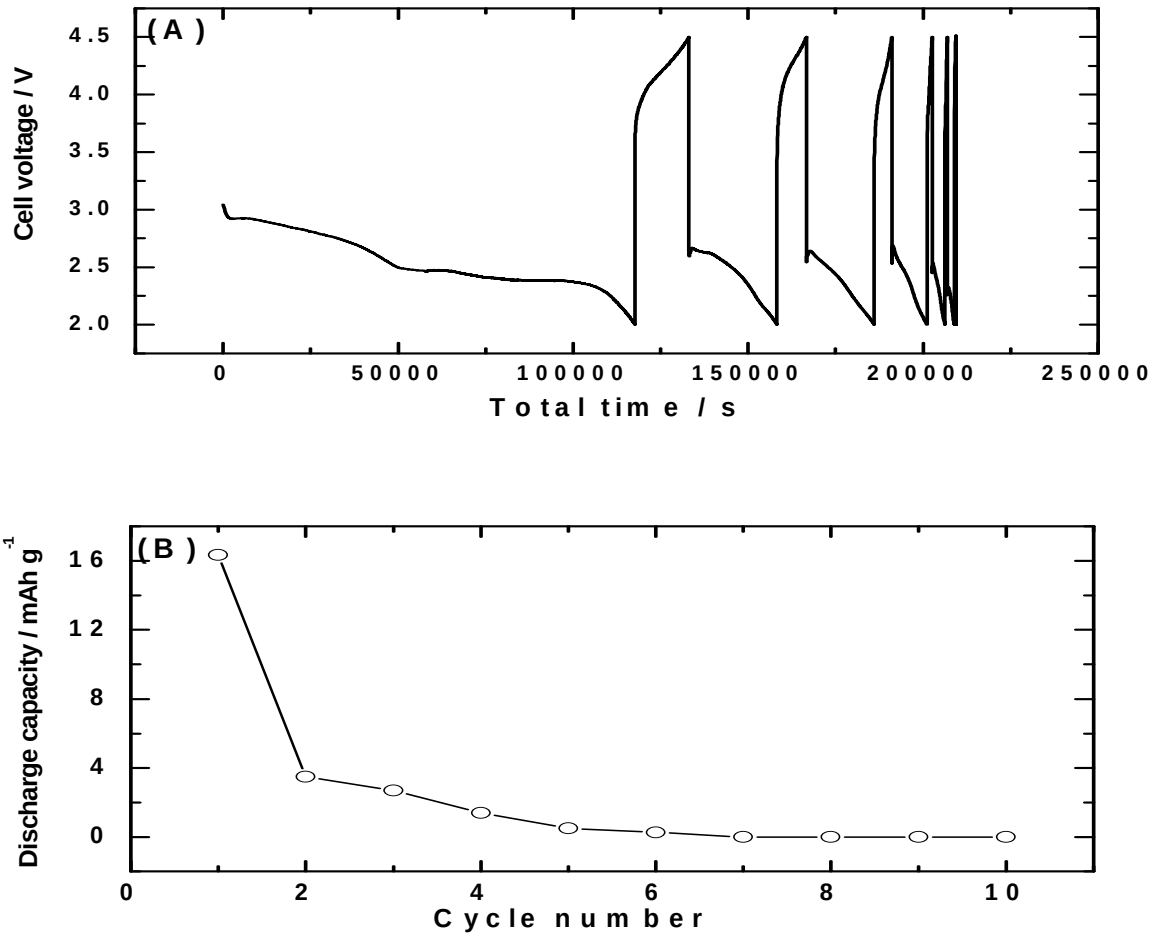

Figure 18: Cell No: TF 185 ;
Active layer carbon : Nil ;
Diffusion layer carbon 153.6 mg ;
Amount of PTFE in active layer : Nil ;
Amount of PTFE in diffusion layer : 30 wt% ;
Discharge – charge current : 0.5 mA;

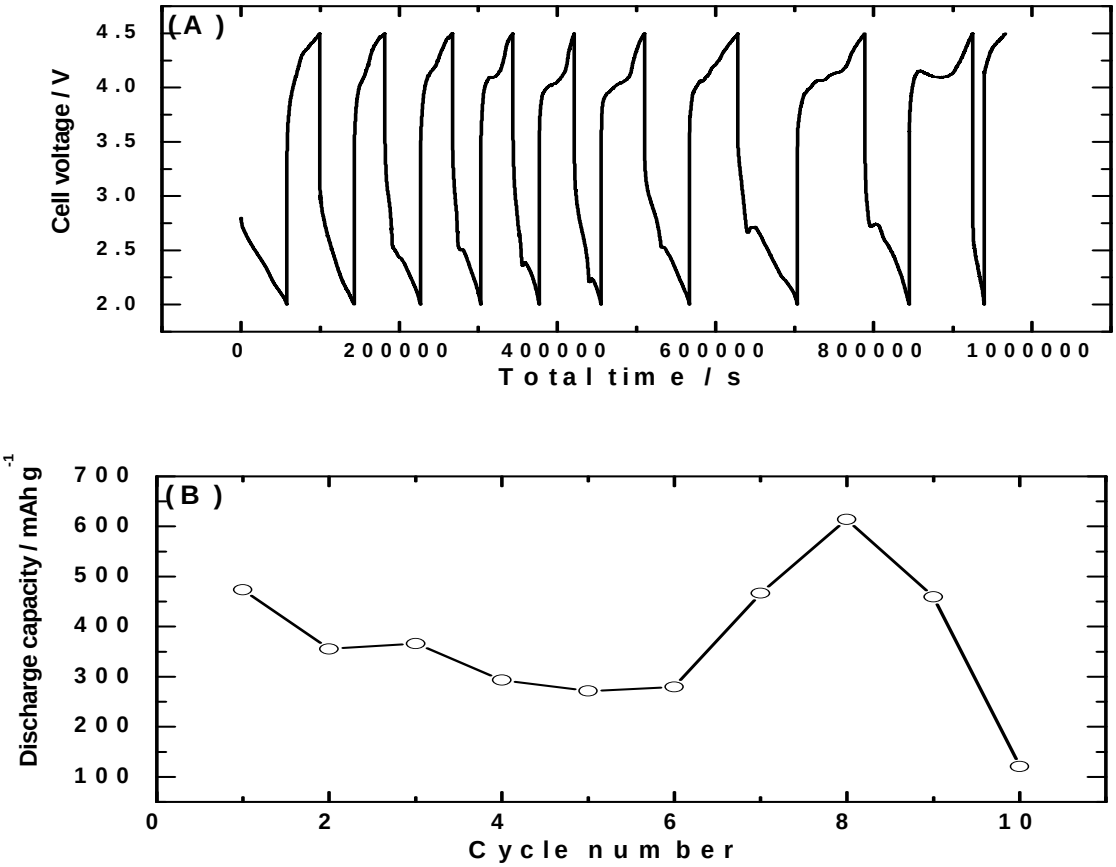

Figure 19 : Cell No: TF 163 ;
Active layer carbon : 17.07 mg;
Diffusion layer carbon : 161.2 mg ;
Amount of PTFE in active layer : 5 wt% ;
Amount of PTFE in diffusion layer : 30 wt% ;
Discharge – charge current : 0.5 mA;

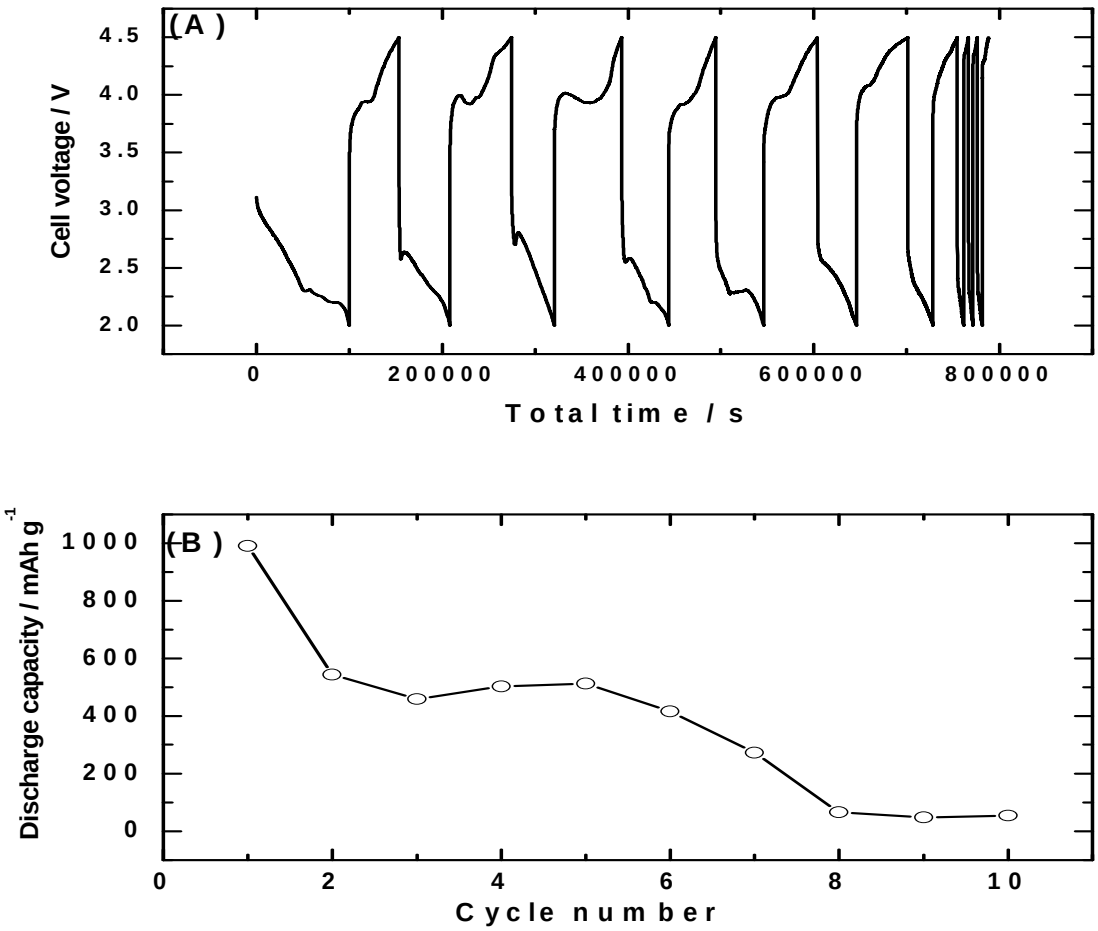

Figure 20: Cell No: TF 180 ;
Active layer carbon : 14.0 mg;
Diffusion layer carbon : 157.8 mg ;
Amount of PTFE in active layer : 7.5 wt% ;
Amount of PTFE in diffusion layer : 50 wt% ;
Discharge – charge current : 0.5 mA;

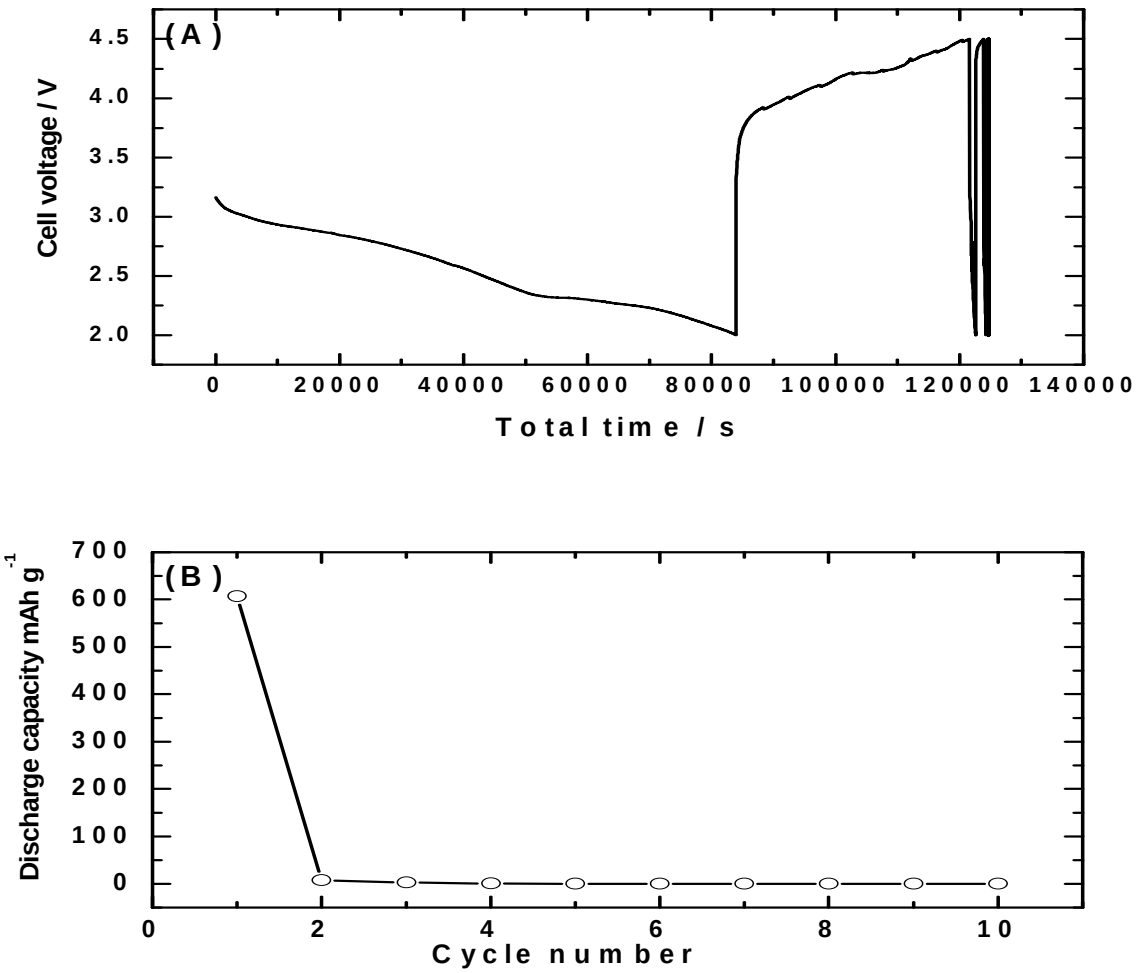

Figure 21 : Cell No: TF 183 ;
Active layer carbon : 19.21 mg;
Diffusion layer carbon : 154.45 mg ;
Amount of PTFE in active layer : 10 wt% ;
Amount of PTFE in diffusion layer : 50 wt% ;
Discharge – charge current : 0.5 mA;

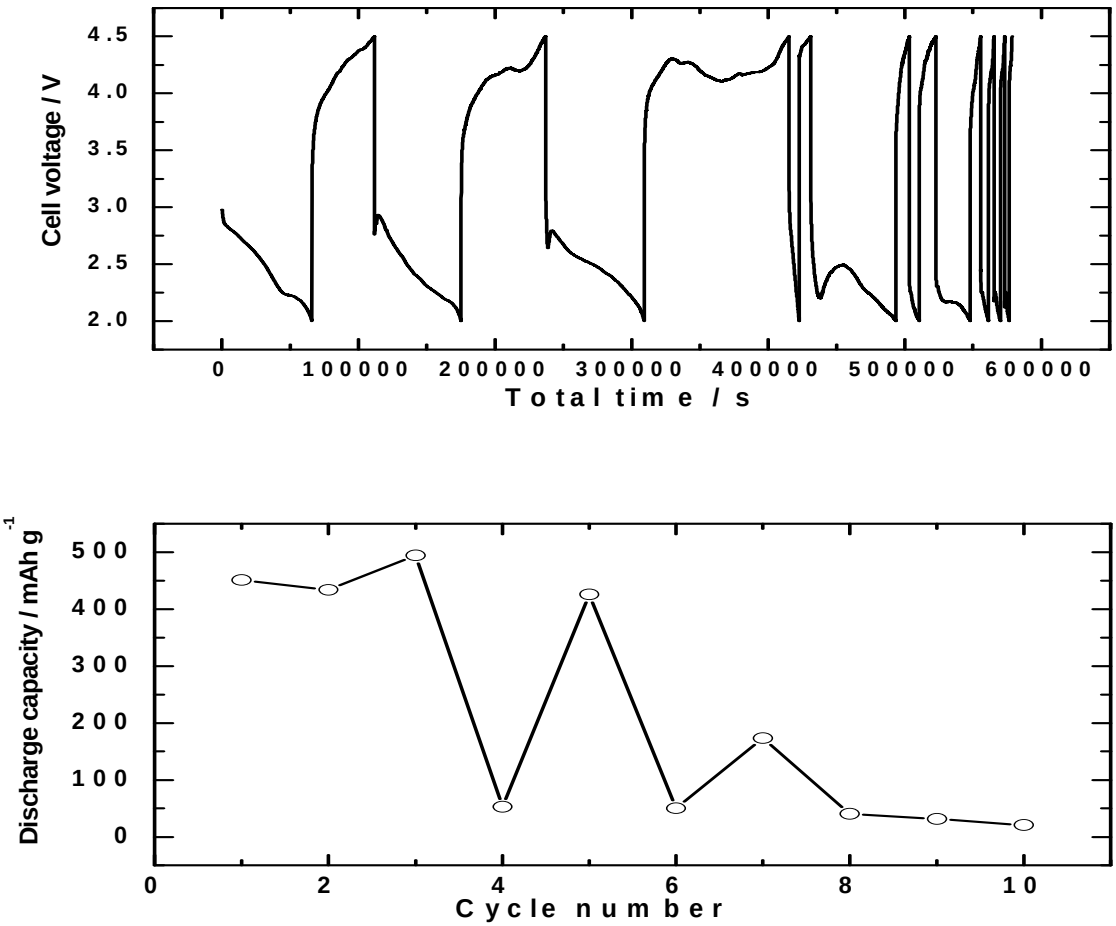

Figure 22: Cell No: TF 187 ;
Active layer carbon : 20.35 mg;
Diffusion layer carbon : 155.32 mg ;
Amount of PTFE in active layer : 30 wt% ;
Amount of PTFE in diffusion layer : 30 wt% ;
Discharge – charge current : 0.5 mA;

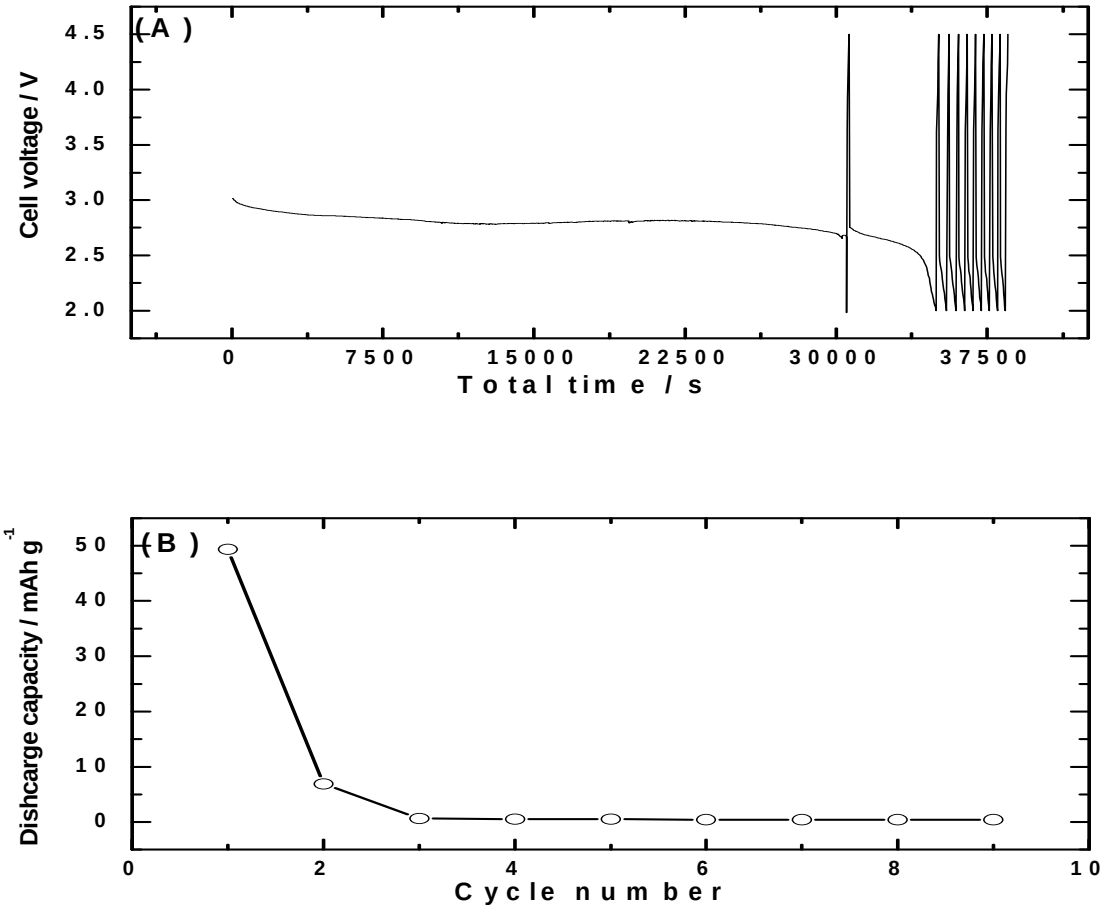

Figure 23 : Cell No: ST 38 ;
Active layer carbon : 17.2 mg;
Diffusion layer carbon : 156.0 mg ;
Amount of PTFE in active layer : 7.5 wt% ;
Amount of PTFE in diffusion layer : 30 wt% ;
Discharge – charge current : 0.2 mA;
Catalyst : α - MnO2
Gel polymer electrolyte

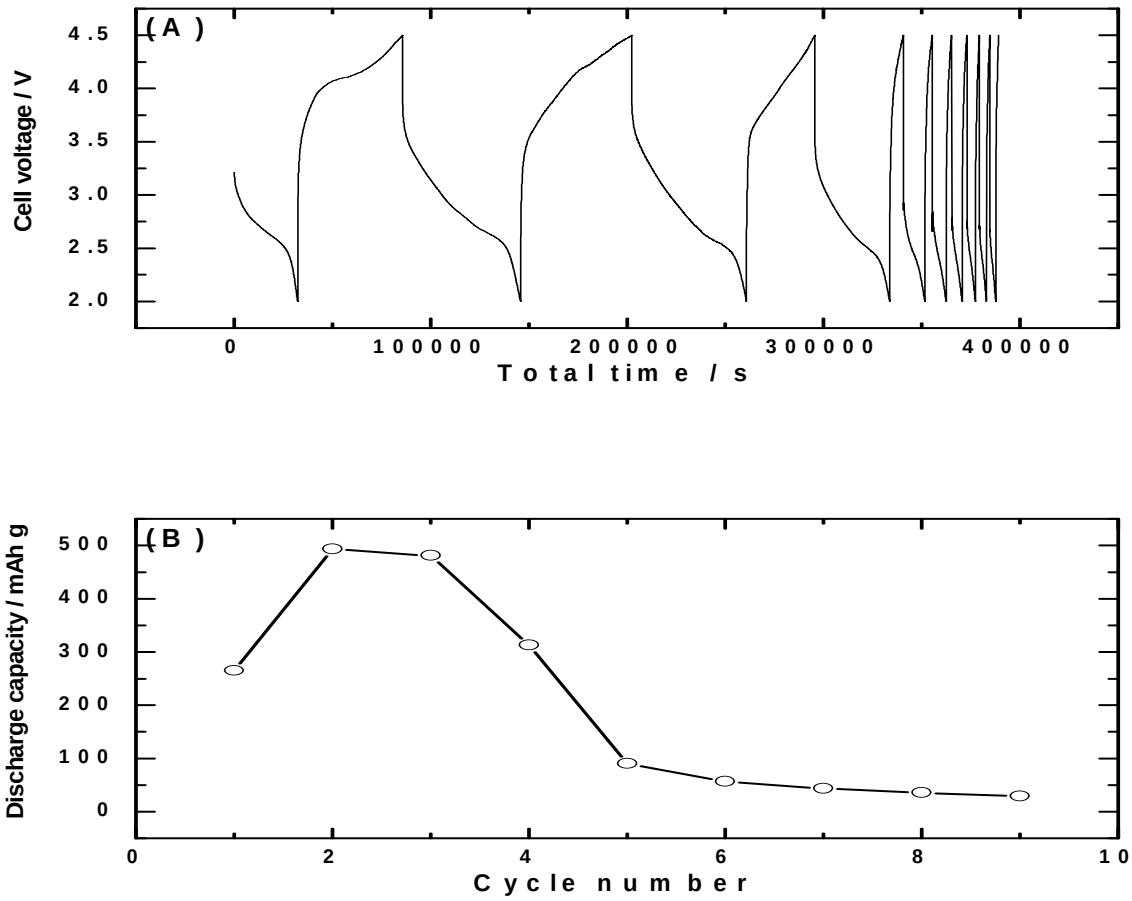

Figure 24 : Cell No: TF 207 ;
Active layer carbon : 16.9 mg;
Diffusion layer carbon : 190.2 mg ;
Amount of PTFE in active layer : 7.5 wt% ;
Amount of PTFE in diffusion layer : 30 wt% ;
Discharge – charge current : 0.2 mA;
Catalyst : α - MnO_2
Propylene carbonate

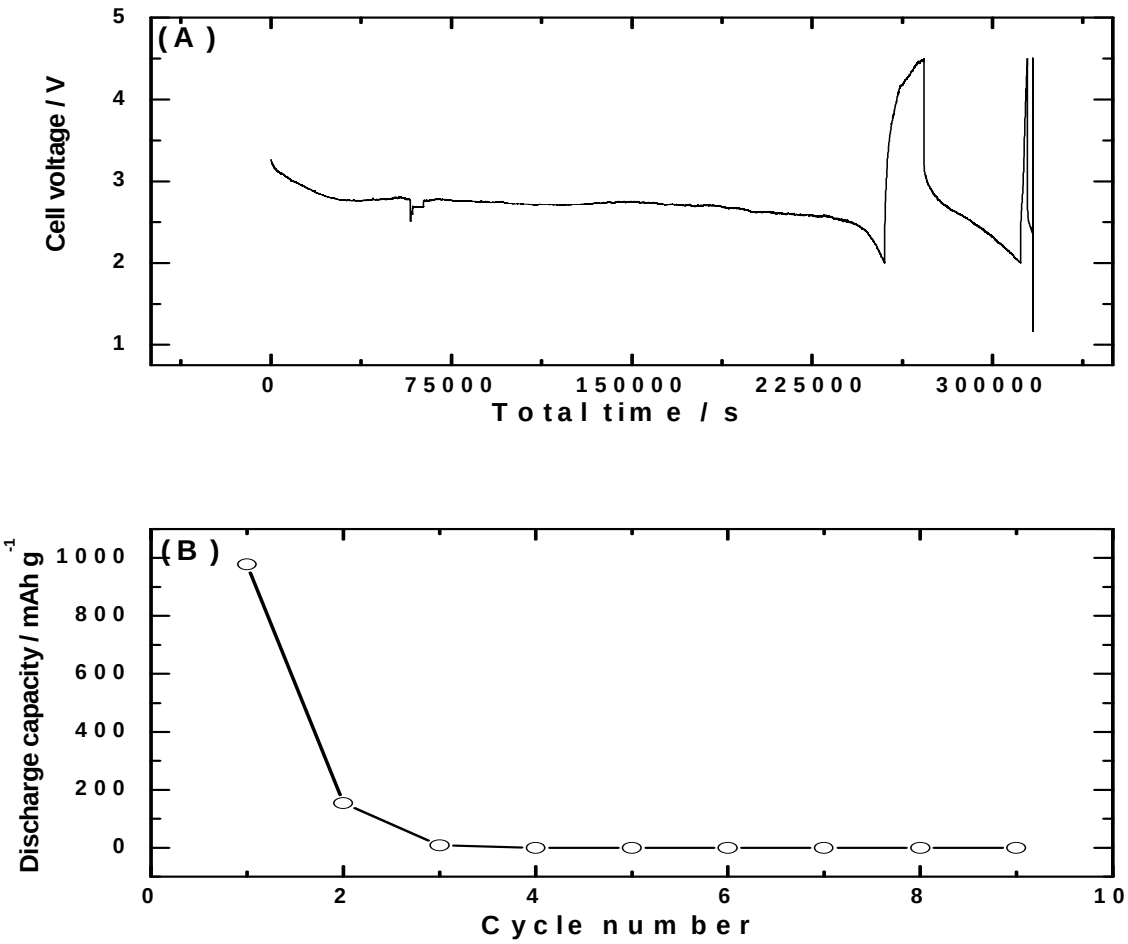

Figure 25: Cell No: ST 40 ;
Active layer carbon : 14.5 mg;
Diffusion layer carbon : 235.2 mg ;
Amount of PTFE in active layer : 7.5 wt% ;
Amount of PTFE in diffusion layer : 30 wt% ;
Discharge – charge current : 0.2 mA;
Catalyst : α - MnO_2
Ethylene carbonate + propylene carbonate

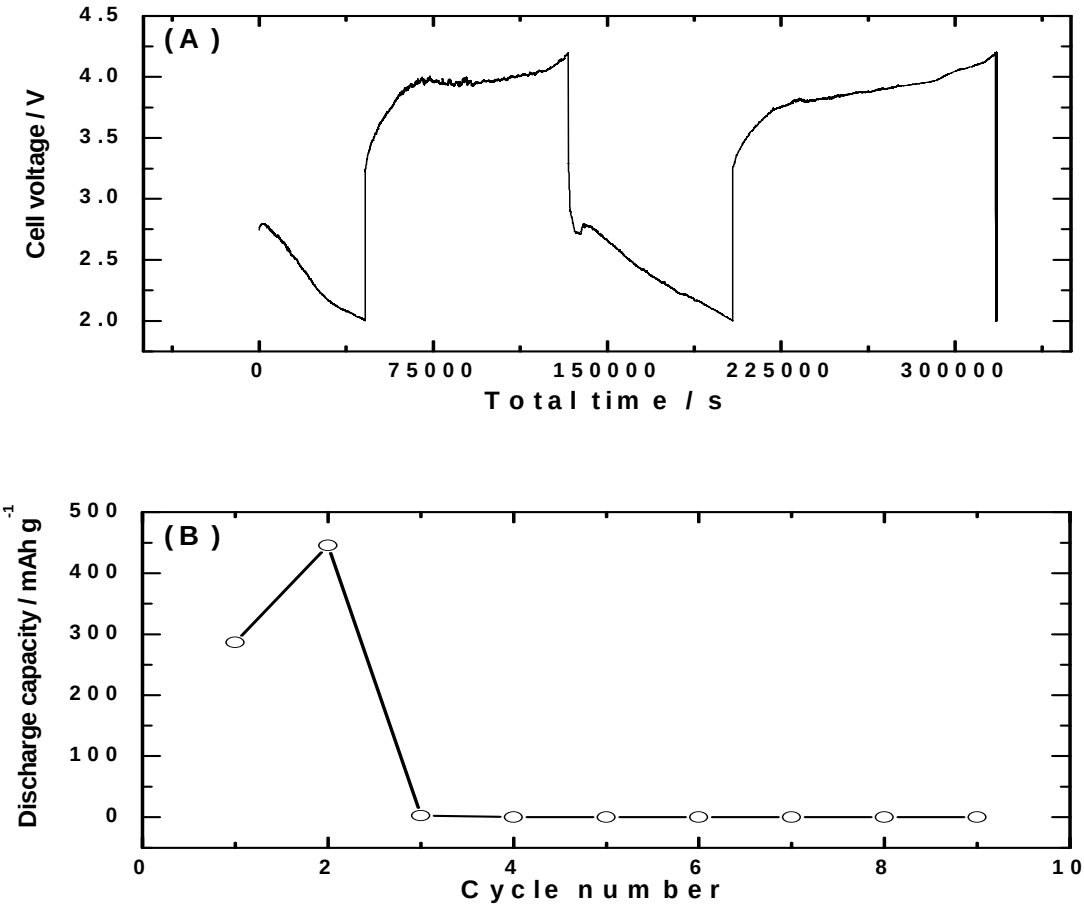

Figure 26 : Cell No: TF 220 ;
Active layer carbon : 22.1 mg;
Diffusion layer carbon : 232.8 mg ;
Amount of PTFE in active layer : 7.5 wt% ;
Amount of PTFE in diffusion layer : 30 wt% ;
Discharge – charge current : 0.2 mA;
Catalyst : α - MnO_2
Propelene carbonate + diethyl carbonate

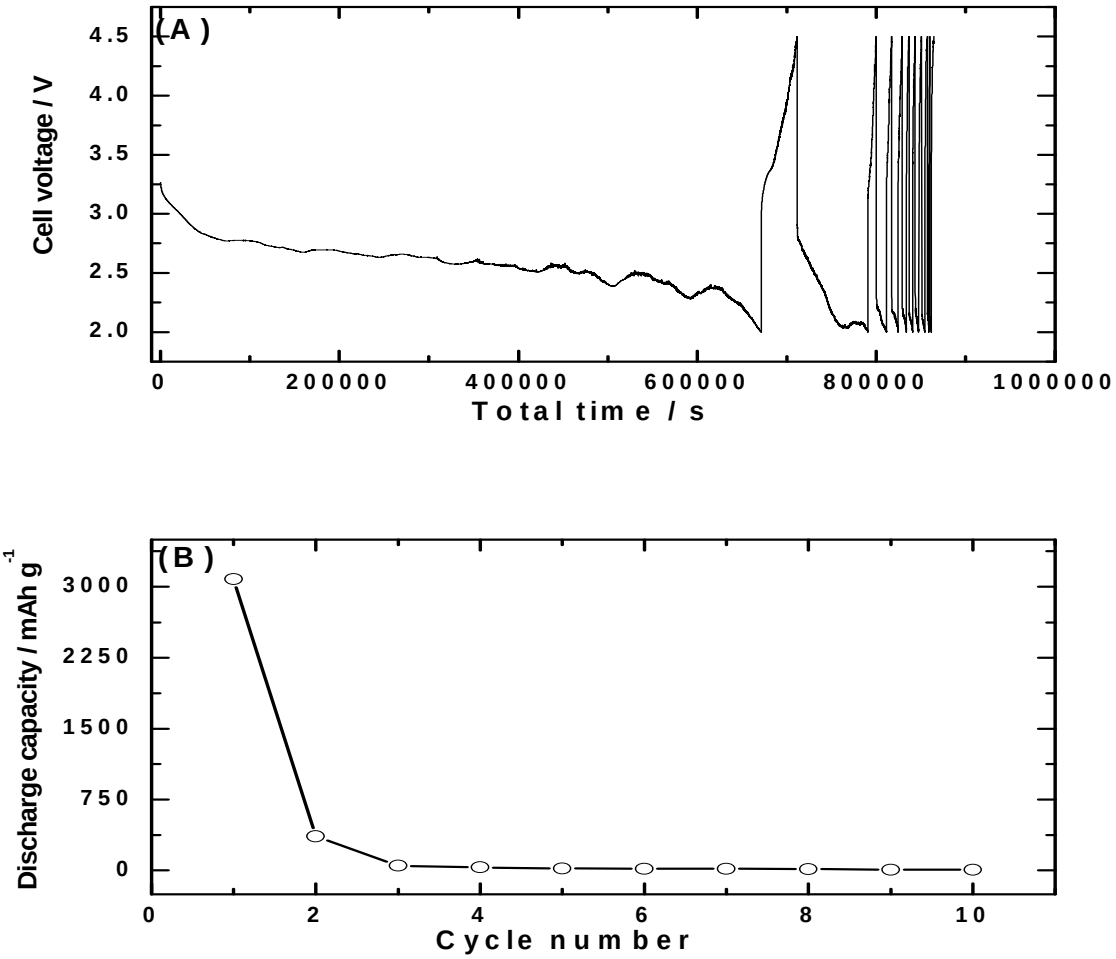

Figure 27 : Cell No: ST 47 ;
Active layer carbon : 12.12 mg;
Diffusion layer carbon : 238.5 mg ;
Amount of PTFE in active layer : 7.5 wt% ;
Amount of PTFE in diffusion layer : 30 wt% ;
Discharge – charge current : 0.2 mA;
Catalyst : α - MnO2
Propylene carbonate + dimethyl carbonate

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Conclusion:

Various aspects related to fabrication of air electrode and assembly of Li-air (or, oxygen) cells are undertaken. Firstly, several carbon samples are screened to fabricate air electrodes, and they are tested by assembling Li-air cells in cell containers suitably made for this purpose. Carbon sample, which is purchased from a China company is found to provide a maximum discharge capacity. Using optimized air electrodes, it is found that a maximum discharge capacity of 3000 mAh/g can be obtained for Li-air cell. This value is one of the highest capacity values reported so far in the literature.

List of Publications: Nil